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OPTIMIZATION OF THE COMPOSITION OF THE FRITTED COMPONENT OF THE RAW MATERIAL MIX OF DURABLE COATINGS

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It is shown that zirconium-free frit should be used to obtain semi-fritted durable glass-crystal coatings, thereby decreasing the total fuel-energy consumption on the production of floor tiles by lowering the synthesis temperature of the frit by 80 – 100°C and decreasing the amount of frit in the raw material mix to 20 – 22.5%.

Key words: semi-fritted coatings, opacifying phases, structure formation, phase composition, frit, raw material mix, floor tiles.

Glass crystalline coatings on ceramics greatly expand the sphere of applications of ceramics in the construction industry and they also make it possible to obtain new technical and functional properties of articles. As a rule, glass crystalline coatings are compositions whose basic properties are due to a crystalline phase or a complex of phases, uniformly distributed in the glass matrix and having micron sizes, which are formed during heat treatment.

The most promising coatings for obtaining by means of fast one-time firing glazed durable ceramic floor tiles with high physical-chemical properties and decorative-aesthetic characteristics are opacified zirconium-containing fritted or semi-fritted glass crystalline coatings with a mat texture. Semi-fritted glazes containing up to 35 – 50%³ frit (USSR Inventor's Certificates Nos. 91659, 1131844, and 1212994), which is characterized by a substantial content of refractory zirconium dioxide, are widely here.

The mechanism of the opacification action of zirconium dioxide is the subject of work by a number of Russian and foreign researchers predominately in the field of fritted coatings. In many of the early studies opacification of glazes was explained by mechanical distribution of the opacifier and it was thought that the degree of opacification is determined only by the grain size of the opacifier and the solubility of the grains in glass. For this reason, an opacifier in the form of zirconium compounds was introduced directly as the frit was ground. In later studies scientists concluded that the dissolved opacifier crystallizes out of the melt of the frit in the form of a finely crystalline phase, giving a more effective opacifying action than when it is introduced during grinding [1 – 3].

According to [1 – 4] the crystallized opacifier passes into melt, and this process is not reversible on cooling. The initial appearance of opacifier crystals is caused by forces acting at the interface between phases, which limit the freedom of motion of the ions and give rise to the formation of centers of crystallization.

It is also well known [2] that the degree of opacification of a glaze is determined not so much by the high content of the crystalline phase as by its total surface area. For this reason, the smaller the particles are, the greater the scattering of light that occurs because of the reflection from them and correspondingly the greater the opacification of the glaze.

Since the mechanism of opacification of semi-fritted coatings differs substantially from that described above for fritted compositions, a study was made to determine the effect of the zirconium component of frit on the degree of the opacification of semi-fritted, mat, glaze coatings.

The compositions developed for the frits R and P in the systems $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{RO} - \text{R}_2\text{O} + (\text{ZrO}_2, \text{B}_2\text{O}_3)$ and $\text{SiO}_2 - \text{ZrO}_2 - \text{RO} - (\text{R}_2\text{O}, \text{Al}_2\text{O}_3, \text{B}_2\text{O}_3)$ for semi-fritted durable coatings [5, 6] are characterized by the substantial content of ZrO_2 — 8.5 – 13%.

The glass crystal coatings obtained with their use are distinguished by high durability (degree 3 – 4) and the required decorative-aesthetic properties (whiteness 85 – 86%, sheen not exceeding 20%). The content of the frits R and P in the raw materials compositions of semi-frit coatings is 22.5 and 20%, respectively.

One way to decrease the consumption of fuel and energy is to lower the melting temperature of the fritted component, which can be achieved by decreasing the quantity of refractory oxides — zirconium dioxide in the case at hand.

To study the possibility of using the zirconium-free frits ZrO_2 as removed from them in steps. Here, the total amount

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³ Here and below — content by weight.

TABLE 1. Frit Composition

Frit	Computed ZrO ₂ com- position, %	Zircobit content in the mix, %	Raw mate- rial compo- sition	Compute ZrO ₂ cont- ent, %	Zircobit content in the mix, %
0R	—	—	K1	6.04	8.59
05R	4.41	6.66	K2	6.14	7.10
R	8.58	12.80	K3	6.24	5.00
0P	—	—	K4	6.86	10.00
05P	6.82	10.33	K5	6.85	7.00
P	12.99	20.30	K6	6.71	5.00

of the zirconium-containing component (zircobit) in the intermediate raw-material composition remained constant, as Table 1 shows.

It should be noted that the MO zircobit (Italy) used contains 32.37% SiO₂, 1.54% Al₂O₃, 65.44% ZrO₂ and its specific surface area is 1.3 – 1.4 m²/g, which can intensify the opacification process and give the required light scattering.

Aside from zircobit conventional materials were used as initial materials for synthesizing frits and semi-fritted coatings: boric acid, dolomite, kaolin, soda ash, chalk, pegmatite, alumina, quartz sand, zinc white, wollastonite, and refractory clay.

A visual assessment of the behavior of finely ground samples of frit and raw-material compositions in the course of heating in the temperature range 800 – 1200°C with step 50°C and soaking at each exposure temperature for 20 min showed that the zirconium-free frit 0R in the interval 1000 – 1200°C forms an amorphous glass, and a glass crystalline structure forms in frits 05R and R in the intervals 1100 – 1200 and 1080 – 1200°C, respectively. Conversely, the zinc-free frit 0P in the interval 1100 – 1200°C possesses a glass crystalline structure, which is supposedly explained by the formation of a pyroxene phase, since the ratio SiO₂ : CaO : MgO in the working composition of a frit approaches the stoichiometric ratio for diopside. As compared with the frits 05R and R, the increase of the formation interval of the glass crystalline structure in frits 05P and P, constituting 1000 – 1200 and 970 – 1200°C, respectively, is probably due to the intensification of the crystallization process as a result of the co-existence of at least two crystalline phases — diopside and zircon.

The crystallization processes occurring during heating of the initial-material mixes of semi-fritted coatings using frits of both series, based on visual assessment, are practically identical. This made it possible to draw a preliminary conclusion that the composition of the initial-materials mix plays a predominate role in the formation of the glass-crystalline structure.

The development of a scientifically validated approach to obtaining glass crystal coatings is based on a determination of the laws of phase formation and systematic comprehensive studies of the interrelation of the structure and prop-

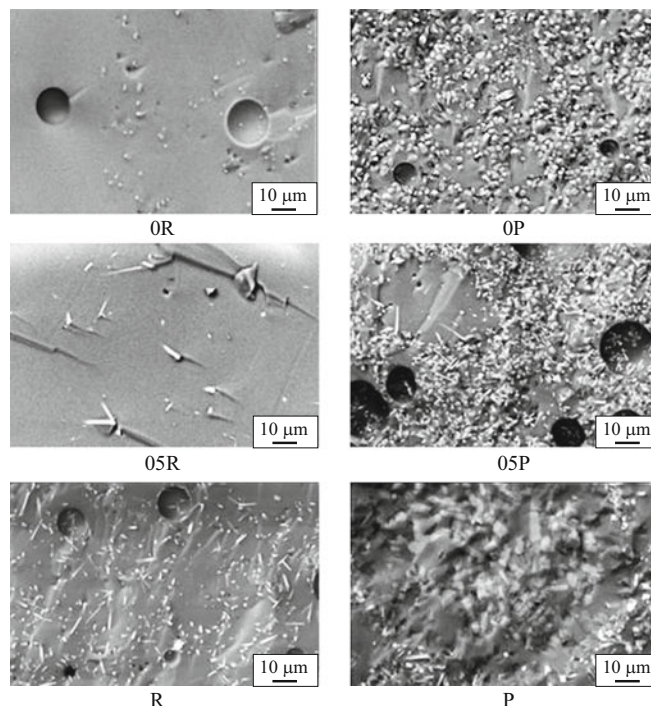


Fig. 1. Electron-microscopic image of the cleavage surface of the frits treated at 1150°C.

erties of coatings for the possibility of regulating them by directed phase formation.

Figure 1 shows electron-microscope images of the cleavage surface of frit samples heat-treated at 1150 ± 10°C. The effect of the ZrO₂ content on the structure-formation processes which occur when frit is heated can be seen clearly.

For example, 0R frit, which does not contain zirconium diopside, forms glass with no indications of phase separation. For 05R frit containing zirconium diopside crystallization with formation of zirconium-containing crystalline phases is seen, and in the case of R frit at 1150 ± 10°C a two-phase structure, formed by a crystalline zirconium-containing and glassy phases, is observed.

The electron-microscope study of cleavage surfaces of samples of heat-treated initial-materials compositions K1 – K3 and K4 – K6 using R and P series frits, respectively, made it possible to conclude that it is precisely the composition of the multicomponent initial-materials mix that plays the main role in the formation of the glass-crystalline structure and that the presence of a fritted component influences the glass-formation processes and promotes earlier appearance of a liquid phase. Ultimately, a temperature close to the optimal firing temperature the coatings of floor tiles under production conditions (1160 ± 10°C) leads to the formation of a glass-crystal structure of the samples K1 – K6, but a more extended crystallization structure of the K4 – K6 samples is observed because of the presence of pyroxene crystalline phase in addition to a zirconium-containing phase.

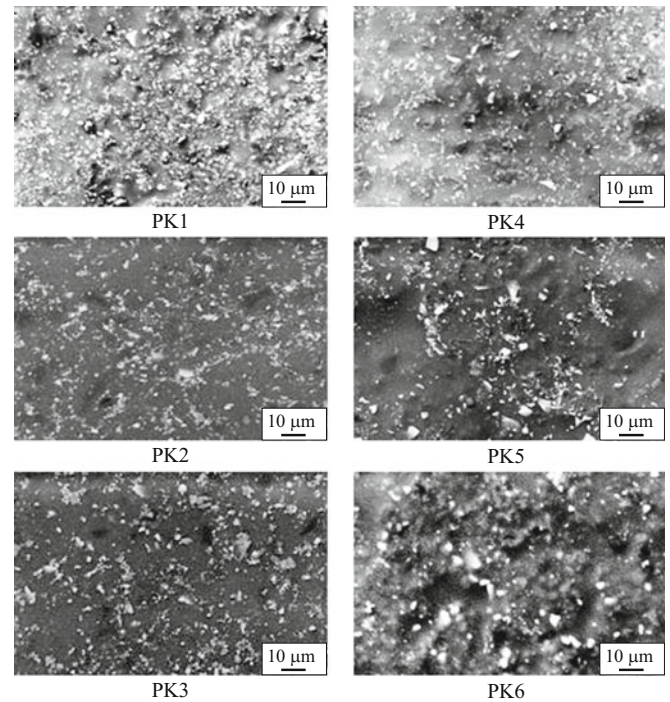
TABLE 2. X-ray Phase Data on Frits

Frit	Phase composition (1150 ± 10°C)	Composi- tion	Phase composition (1150 ± 10°C)
0R	Amorphous (glass)	K1	Zircon (ZrSiO_4), quartz ($\alpha\text{-SiO}_2$), anortite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), corundum ($\alpha\text{-Al}_2\text{O}_3$)
05R	Zircon (ZrSiO_4)	K2	Zircon (ZrSiO_4), quartz ($\alpha\text{-SiO}_2$), anortite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), corundum ($\alpha\text{-Al}_2\text{O}_3$)
R	Zircon (ZrSiO_4)	K3	Zircon (ZrSiO_4), quartz ($\alpha\text{-SiO}_2$), anortite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), corundum ($\alpha\text{-Al}_2\text{O}_3$)
0P	Diopside ($\text{CaMgSi}_2\text{O}_6$)	K4	Zircon (ZrSiO_4), baddeleyite (ZrO_2), diopside ($\text{CaMgSi}_2\text{O}_6$), corundum ($\alpha\text{-Al}_2\text{O}_3$), quartz ($\alpha\text{-SiO}_2$)
05P	Diopside ($\text{CaMgSi}_2\text{O}_6$), zircon (ZrSiO_4)	K5	Zircon (ZrSiO_4), baddeleyite (ZrO_2), diopside ($\text{CaMgSi}_2\text{O}_6$), corundum ($\alpha\text{-Al}_2\text{O}_3$), quartz ($\alpha\text{-SiO}_2$)
P	Diopside ($\text{CaMgSi}_2\text{O}_6$), zircon (ZrSiO_4), $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$	K6	Zircon (ZrSiO_4), baddeleyite (ZrO_2), diopside ($\text{CaMgSi}_2\text{O}_6$), corundum ($\alpha\text{-Al}_2\text{O}_3$), anortite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), quartz ($\alpha\text{-SiO}_2$)

X-ray phase investigation gave concrete information on phase formation during heat-treatment of frits and initial-materials mixes with the use of the frits. The results are presented in Table 2.

Thus, phase formation in series R frits in the sequence 0R → 05R → R is distinguished by the fact that the first one is a glass, and the second and third contains zircon as the main and only crystalline phase, while with heat-treatment of series P frits in the sequence 0P → 05P → P the first one is already crystallized and is represented by diopside, the second one is represented by zircon and diopside presumably in equal quantities, while the third contains, aside from the phases enumerated, the compound $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$.

The heat-treatment of the raw-materials mixes K1 – K6 at the indicated temperature results in the formation of a glass crystal structure. The phase composition of the mixes K1 – K3 is represented by zircon (ZrSiO_4), quartz ($\alpha\text{-SiO}_2$), and anortite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), and corundum ($\alpha\text{-Al}_2\text{O}_3$), while the phase composition of the mixes K4 – K6 is represented by zircon (ZrSiO_4), baddeleyite (ZrO_2), diopside ($\text{CaMgSi}_2\text{O}_6$), anortite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), corundum ($\alpha\text{-Al}_2\text{O}_3$), and quartz ($\alpha\text{-SiO}_2$).

**Fig. 2.** Electron-microscopic image of the surface of semi-fritted glazed coatings.

Thus, the phase formation process is practically identical in the initial-materials mixes obtaining using series R and P frits. This indicates that the initial materials play the predominant role; their quantity is 77.5% in the mixes K1 – K3 and 80% in the mixes K4 – K6.

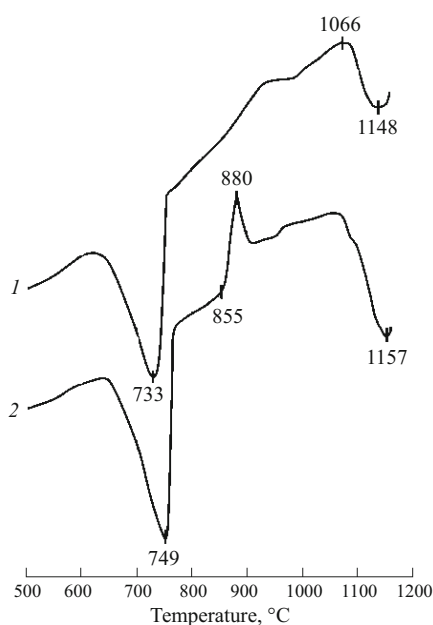
At Keramin JSC (Minsk) the glaze coatings PK1 – PK6, which have a uniform glass-crystalline structure (Fig. 2) with a uniform distribution of the crystals of the opacifying phases, were obtained from the initial-materials mixes K1 – K6. For coatings using zirconium-free frits (PK1 and PK4) the sizes of the ZrSiO_4 crystals do not exceed 1 – 2 μm and the light-scattering power reaches 400 – 450 cm^{-1} , which attests to a high degree of opacification. A characteristic feature of the glass-crystal coatings is their mat, silky surface texture and high whiteness.

The physical-chemical and decorative-aesthetic characteristics of the coatings are presented in Table 3. Analysis of the indicators of the properties made it possible to recommend as the optimal coatings PK1 and PK4, synthesized using zirconium-free frits OR and OP, respectively, but in the latter case there is some decrease of the microhardness and degradation of the sheen and whiteness.

It is our opinion that this is due to the active formation of diopside, whose total quantity in the coating consists of the diopside in the fritted component and in the non-fritted component; this is confirmed by the DTA data presented in Fig. 3. Thus, no exothermal effect peaking at 880°C is observed in the curve 1 which corresponds to the coating mix PK1; such an effect is present in the curve 2 corresponding to the crystallization of diopside when the mix PK4 is heated.

TABLE 3. Post-Firing Characteristics of Coatings

Indicator	Post-firing properties of coatings					
	PK1	PK2	PK3	PK4	PK5	PK6
Firing temperature, °C	1150 ± 10	1150 ± 10	1150 ± 10	1150 ± 10	1150 ± 10	1150 ± 10
Microhardness, MPa	9560	9400	9100	7590	7320	7250
Mohs hardness	7 – 8	7 – 8	7 – 8	6 – 7	6 – 7	6 – 7
Durability	4 – 3	4 – 3	4 – 3	3	3	3
CLTE, 10 ⁻⁷ K ⁻¹	68.26	69.59	69.92	69.78	69.95	70.40
Heat-resistance	125	125	125	125	125	125
Texture	Mat silky					
Sheen, %	14	16	17 – 18	15	17	20
Whiteness, %	83	80	80	68	70	71
Chemical stability	Satisfied normative-technical documentation					

**Fig. 3.** DTA curves for the raw materials compositions PK1 (1) and PK4 (4).

These data correlate with the results of x-ray phase analysis of the surface of the coatings whose phase composition is represented by relic zircon (ZrSiO_4), corundum ($\alpha\text{-Al}_2\text{O}_3$), and anortite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) in coating PK1, and additional crystalline phases are represented by diopside ($\text{CaMgSi}_2\text{O}_6$) and akermanite ($\text{Ca}_2\text{AlSi}_7\text{O}_7$) in coating PK4.

The electron-microscope image of the surfaces of the coatings PK1 and PK4 (see Fig. 2) attests to a more uniform even glass crystal structure of the first coating, and the zircon crystals are smaller (1 – 3 μm). The structure of the PK4 coating is less dense because of the presence of additional pyroxene phases with a chain-like structural motif and larger zircon crystals, reaching 5 – 7 μm , not entirely uniformly distributed in the glassy matrix. In addition, the diopside (monoclinic, colorless, or grayish) is not an opacifier and be-

cause of its crystal-chemical features can open up the structure of the glass crystal coating because of the simultaneous presence of simple coordination compounds (corundum), framework (α -quartz), and island (zircon).

The more active process of formation of the glassy phase occurs in the temperature interval 1050 – 1150°C in coating PK4, as the DTA curve (see Fig. 3) shows and, together with what has been indicated above, also diminishes the properties.

The investigations confirmed that it is desirable to use zirconium-free frits as the fritted component for obtaining high-durability semi-fritted glass crystalline coatings, which decreases the total fuel and energy consumption in the production of floor tiles because of a decrease of the synthesis temperature of the frit by 80 – 100°C. The coatings developed are well-opacified and white, have a mat texture and durability 3 – 4, and can be tinted with pigments with a wide range of colors and widely used in locations with high foot traffic.

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